

Encapsulation of Hydrophilic Dyes with Polystyrene Using Double Miniemulsion Technique

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ABSTRACT: Hydrophilic dyes, reactive brilliant red K-2BP (C.I. Reactive red 24), acid fuchsin (C.I. Acid violet 19), and cationic brilliant red 5GN (C.I. Basic red 14), have been encapsulated into hydrophobic polystyrene (PS) latex particles using double miniemulsion technique. In this method, the water droplets containing dyes were first suspended in octane/styrene phase using lipophilic emulsifiers to form a primary miniemulsion. This miniemulsion was further dispersed in water and miniemulsified, fol-

lowed by polymerization at high temperature to form dye/PS core-shell colorants. Experimental results show that this technique can cause as high as 80% of encapsulation efficiency for all three dyes, and obviously improve the water-proofing property and photostability of organic dyes. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3615–3622, 2011

Key words: hydrophilic dyes; encapsulation; miniemulsion polymerization; water-fastness

INTRODUCTION

With broad color range and great strength, dyestuffs have been widely used as the colorants of inks,^{1,2} coatings,³ etc. Because of the environmental restriction, waterborne inks and coatings developed quickly in the past years, giving a great demand on waterborne colorants. Generally, due to the poor water-dispersibility, oil-soluble dyes have to be encapsulated into polymer latex particles to meet the application in waterborne system,^{4,5} while water-soluble dyes can be directly used as the waterborne colorants. However, they are very poor in water-fastness and light-fastness, which results in a quick fading and/or low image resolution of the end products. Therefore, further improvements of water soluble dyes using effective strategies are still necessary.

Encapsulation of oil-soluble dyes into polymer latex particles have been largely reported via emulsion

polymerization,^{6,7} interfacial polymerization,⁸ and especially miniemulsification polymerization.^{9–12} But encapsulation of water-soluble dyes with polymer shell still remains a challenge. Since water-soluble dyes can not be dissolved or dispersed in hydrophobic monomers directly, they need to be dissolved in water and then encapsulated by polymer. Namely, encapsulation of aqueous core has to be involved for the water-soluble dyes.

In recent years, fabrication of nanocapsules with aqueous core is paid great attention in foods and pharmaceuticals with controlled release property, in which double emulsion technique is frequently adopted. For instances, Nihant et al.¹³ fabricated bovine serum albumin-loaded poly(lactic acid) micro-particles and Zambaux et al.¹⁴ prepared human serum albumin-loaded poly(lactic acid) nanoparticles via double emulsion solvent evaporation (DES-E) method. Cui et al.¹⁵ also made melittin-loaded poly(DL-lactic acid) or poly(DL-lactic-co-glycolic acid) microspheres using DES-E technique. Benichou et al.¹⁶ encapsulated Vitamin B₁ into whey protein isolate/polysaccharide complexes using W/O/W double emulsions method. Cohen-Sela et al.¹⁷ fabricated alendronate-loaded poly(lactide-co-glycolide) nanoparticles with high encapsulation efficiency using double emulsion solvent diffusion technique. However, encapsulation of the aqueous core containing hydrophilic dyes, to improve water-fastness and light-fastness of the dyes, has not been reported yet.

In this article, double emulsification technique was employed to encapsulate hydrophilic dyes with different molecular structures into polystyrene (PS)

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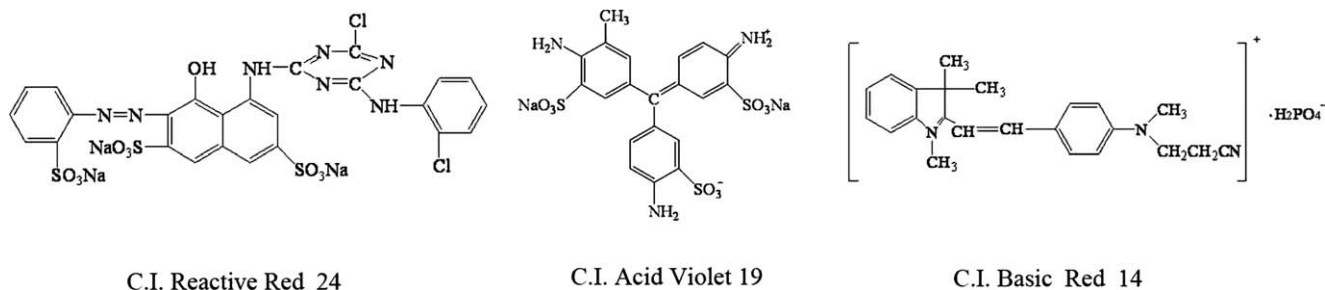


Figure 1 Chemical structure of dyes.

latex particles. In this method, water droplets containing hydrophilic dyes were suspended in octane/styrene and miniemulsified in the presence of lipophilic emulsifiers to form a primary miniemulsion. After that, the primary emulsion was further dispersed in water and miniemulsified, followed by polymerization at high temperature. The stability of the formed double miniemulsion and the encapsulation efficiency of dyes were examined, the obtained dye/PS composite latex colorants had excellent water-fastness and photostability.

EXPERIMENTAL SECTION

Materials

Dyes: reactive brilliant red K-2BP (RBR, C.I. Reactive red 24), acid fuchsin (AF, C.I. Acid violet 19) and cationic brilliant red 5GN (CBR, C.I. Basic red 14), were of chemical grade and obtained from Luoqing Dyeing Chemical (Shanghai, China). Their chemical structures are shown in Figure 1. Styrene (St), 2,2'-azobis(isobutyronitrile) (AIBN), sodium lauryl sulfate (SLS), polyoxyethylene octylphenol ether (OP-10), sorbitan monooleate (Span 80), octane, ethanol, and tetrahydrofuran (THF) were purchased from Sinopharm Group Chemical Reagent (Shanghai, China) and used as received, except that St was distilled under reduced pressure before use. Hexadecane (HD) was obtained from Fluka and used as received. Deionized water was prepared in our lab.

Encapsulation of dyes with polystyrene

The encapsulation of dyes with polystyrene (PS) was typically carried out as follows: four kinds of solutions, as shown in Table I, were first prepared. Solution A (namely aqueous dye solution) was mixed with Solution B under vigorously stirring, to obtain a water-in-oil preemulsion. The preemulsion was charged with Solution C and further homogenized for 120 s using an ultrasonic homogenizer (Scientz-IIID, power: 950 W, Scientz Biotechnology, Ningbo, China), operated at 90% amplitude, 3-s

pulse on and 3-s pulse off cycles and cooled with an ice-water bath, to form primary water-in-oil (W/O) miniemulsion. Afterward, the primary W/O miniemulsion was charged into Solution D, and vigorously stirred for 10 min. The mixture was further ultrasonified for 30 s using the ultrasonic homogenizer, operated at the same parameters as above but with 50% amplitude, resulting in a water-in-oil-in-water (W/O/W) double miniemulsion. The double miniemulsion was transferred into a four-necked flask and deoxygenated by purging with nitrogen, and then polymerized at 70°C for about 10 h. For the sake of comparison, dye-free PS latices were prepared by the same procedure, except that the dye was not included in the recipe. It should be noted that the mixed surfactants, OP-10/Span 80 in primary miniemulsion and SLS/OP-10 in double miniemulsion, were adopted based on their HLB values and optimized from a series of experiments. Separated usage of Span 80, OP-10 or SLS was found unsuccessful for preparation of stable primary or double miniemulsions herein.

RBR/PS latex was adopted as an example for determination of the molecular weight of PS shell. Gel permeation chromatography analysis indicated that PS has weight-average molecular weight of $1.2 \times 10^5 \text{ g mol}^{-1}$ and polydispersity of 4.4 using narrow PS as the standard.

TABLE I
Typical Recipe for Encapsulation of Dyes with Polystyrene

Solutions	Ingredients	Weight (g)
A	Water	1
	Dye	0.1
	OP-10	0.04
B	Octane	4
	Span 80	0.2
C	St	5
	AIBN	0.11
	HD	0.25
D	Water	40
	SLS	0.05
	OP-10	0.15

Characterization

UV-visible spectra

The absorption spectra were recorded on a UV-visible spectrophotometer (UV 1800 PC, Shanghai Mapada, China) at a temperature of $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$.

Morphology

A transmission electron microscope (TEM, Hitachi H-600, Japan) and a field-emission TEM (JEM-2100 F, JEOL, Japan) were used to observe the morphologies of pure PS latex and dye-loaded PS latices. Each sample was dropped onto carbon-coated copper grids and dried at room temperature before examination.

Particle size and its distribution

The particle size and its distribution were determined using a particle size analyzer (N4 Plus, Beckman Coulter, USA). SDP mode was employed to analyze the data.

Encapsulation efficiency

Diluted dye solutions in the mixture of water and THF (water-to-THF volume ratio: 1/4) with various concentrations were prepared and underwent absorption spectroscopy analysis with a UV-visible spectrophotometer (UV 1800 PC, Shanghai Mapada, China). The absorption intensity of the maximum peaks (at wavelength of 542, 554, and 532 nm for RBR, AF, and CBR dye, respectively) as a function of dye concentration was adopted to establish calibration curves. The dye-loaded polymer latices were centrifuged (6000 rpm) and washed with ethanol to remove the dissociated dye molecules. The obtained particles were dried overnight in an oven at 80°C . The dried particles were dissolved in the mixture of water and THF (water-to-THF volume ratio: 1/4) based on a concentration of 0.02 mg mL^{-1} . Then the visible spectra of dye solutions were recorded by the UV-visible spectrophotometer. The actual dyes concentration (C , mg mL^{-1}) in THF/water was obtained from the calibration curve based on the absorption intensity of the maximum peaks of the spectrum, and thus the encapsulation efficiency (E , the mass of the dyes inside PS particles dividing the total mass of the dye in the latex) can be calculated as follows:

$$E(\%) = \frac{C}{0.02 - C} \cdot \frac{M_{\text{st}}}{M_{\text{dye}}} \times 100$$

where M_{st} and M_{dye} are the weights of St and dye in the recipe, respectively.

Water-fastness

To remove the dissociated dyes in aqueous phase, the as-synthesized dye/PS composite latex colorants were dialyzed until the dialyzate became colorless, and then loaded in the ink cartridge of a fountain pen and wrote words on printing papers. For comparison, the mixture of dyes with pure PS latex was also used as the inks of the fountain pen. The papers with printed words were dried at room temperature for 1 day and then immersed into water for 5–30 min. The disappearance of the words was used to evaluate the waterproof ability of the prepared colorants.

Photostability

The photostability of pure dyes and the dye/PS latex colorants were examined by UV irradiation experiments. Aqueous dye solutions with a concentration of 2 mg mL^{-1} and dye/PS lattices with the same dye concentration were prepared. All of the samples were placed in a UV crosslinker (wavelength 365 nm, 3.1 mW cm^{-2} , Model XLE-1000, Spectroline, USA). The absorption spectra were measured as a function of UV irradiation time.

RESULTS AND DISCUSSION

Encapsulation of water-soluble dyes

Stability of the double miniemulsion

Because of the existence of osmotic pressure, dye molecules tend to diffuse from the interior of the primary W/O miniemulsion droplets to the continuous aqueous phase of the double miniemulsion, resulting in the decrease of the system stability and encapsulation efficiency of dyes. To examine the diffusion of dyes, the primary miniemulsion with various concentrations of emulsifiers were charged into the water containing SLS and OP-10. No stirring or ultrasonification was employed. Herein, RBR dye was used as an example.

Figure 2 displays the appearance and the absorbance spectra of the bottom water layer for the mixtures after stored for 7 days. The upper layer is RBR dye-loaded primary W/O miniemulsion and the bottom one is water with hydrophilic surfactants. Red water layer [Fig. 2(a)] and strong absorption intensity in visible range [Fig. 2(f)] are observed for the sample with 2 wt % concentration of lipophilic emulsifier based on the weight of octane. The color of the bottom aqueous phase becomes light pink [Fig. 2(b)] and the absorption intensity remarkably decreases [Fig. 2(f)] when the concentration of the lipophilic emulsifier increases to 4 wt %, indicating less dyes have transferred from the primary W/O

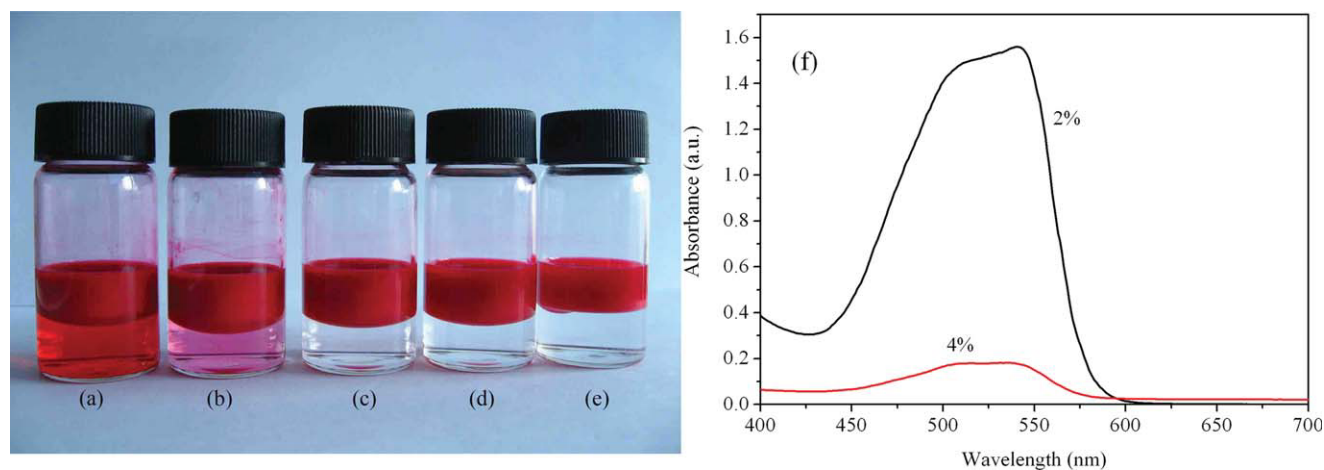


Figure 2 The appearance of the mixtures of water (including hydrophilic emulsifier) and primary miniemulsion with various concentration of lipophilic emulsifier after stored for 7 days: (a) 2, (b) 4, (c) 6, (d) 8 and (e) 10 wt % (based on the weight of octane) and (f) the absorbance spectra of RBR in the bottom water layer for the cases with 2 and 4 wt % of lipophilic emulsifier. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

miniemulsion to water phase. Phase separation in the primary W/O emulsion was also observed for these two cases, which could be regarded as the cause of the transfer of dyes. As the concentration of lipophilic emulsifier is up to 6 wt % or higher, the bottom aqueous phase is colorless and no phase separation in the primary miniemulsion is observed [Fig. 2(c–e)], which does not change even after 1 month of storage. This suggests that no dyes can enter into water phase at relatively high concentration of lipophilic emulsifier. On the basis of these experiments, we can deduce that the dyes entrapped in the primary miniemulsion do not transfer into the continuous aqueous phase once the double miniemulsion is stably formed. The extremely low solubility of water and dyes in oil phase (mainly consisting of octane and St) and thus low penetration ability of dyes should be responsible for the low transfer of dyes.

The aggregate state of the dyes in the water droplet of the primary miniemulsion would be another factor to reduce the diffusion of dyes, which can be evidenced from the absorption spectra of the aqueous dye solutions as shown in Figure 3. An absorption peak at wavelength of 535 nm is observed at low RBR concentration (1×10^{-5} M to 5×10^{-5} M), and the absorption intensity as a function of RBR concentration obeys Beer's law, suggesting no aggregates in these solutions. However, the absorption peak red-shifts to 541 and 556 nm at RBR concentration of 1×10^{-4} M and 1×10^{-3} M, respectively, and their absorption intensities substantially deviate from Beer's law. A new peak at ~ 431 nm even appears at RBR concentration of 1×10^{-3} M. All these facts reveal that RBR dye aggregates would form at high RBR concentration.^{18–20} In our studies, the RBR concentration in water droplets is as high

as 2×10^{-3} M, meaning that RBR dyes in the primary miniemulsion is actually existed in the form of aggregates. In comparison with dye molecules, dye aggregates are more difficult to transport across the oil layer and thus contribute to the stability of the obtained double miniemulsion.

Morphology and size of the dye/PS composite latex colorants

Figure 4 demonstrates the TEM images of pure PS latex particles and RBR dye-loaded PS particles. Pure PS particles are spherical with a diameter of ~ 120 nm and relatively narrow size distribution. However, once 2 wt % RBR dye was included, two kinds of latex particles, one with sizes enlarging to around 250 nm and another with sizes approaching to the pure PS latex particles, are observed. Field

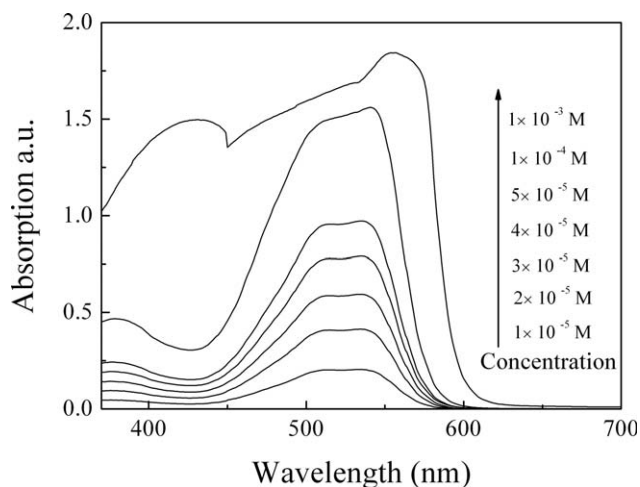


Figure 3 The absorption spectra of aqueous RBR solutions with various concentrations.

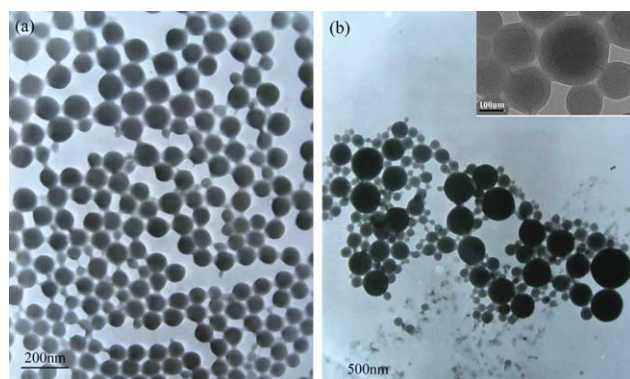


Figure 4 TEM images of (a) pure PS latex particles and (b) RBR/PS composite latex particles. Inset: field emission TEM image of RBR/PS composite latex particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

emission TEM observation [the inset image of Fig. 4(b)] indicates that the big particles possess distinct core-shell structure, in which the core should belong to the mixture of RBR aggregates and OP-10/Span 80 surfactants, and the shell should be PS. Considering the evaporation of small molecules during sample preparation for TEM observation, the core of the big particles in latex should additionally contain water while the shell should be the swelled PS with octane and HD. Whatever, core-shell structure did not appear for the small particles. We inferred that the small particles may be pure PS particles that should be formed through fusion–fission of primary W/O miniemulsion droplets during ultrasonication (see the formation mechanism discussed below). Encapsulation of other two hydrophilic dyes, AF and CBR, with PS was conducted with the same process as that used for RBR dyes. Figure 5 presents the TEM images of the obtained dye-loaded PS particles. Similar to RBR/PS latex, both AF/PS and CBR/PS latex colorants have two kinds of latex particles. Therefore, water-soluble dye molecules had been successfully encapsulated into PS matrices in spite

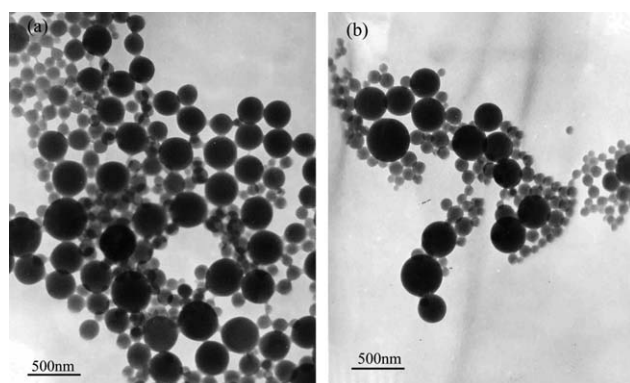


Figure 5 TEM images of (a) AF/PS composite latex particles and (b) CBR/PS composite latex particles.

of their chemical structures, indicating the universal character of the double miniemulsion technique for the encapsulation of hydrophilic dyes into polymer particles.

The sizes of the obtained latex colorants and pure PS latex were also analyzed by dynamic light scattering (DLS) and plotted in Figure 6. It can be seen that pure PS latex has small mean size and narrow particle size distribution (namely, low SD). All latex colorants have relatively big mean sizes and wide particle size distributions (namely, high SD), being consistent with TEM observations. Especially, remarkable increases of particle size and its distribution were revealed for AF/PS and CBR/PS lattices. However, the particle size distributions of the latex colorants are all unimodal, and the two kinds of latex particles as described above can not be distinguished from the curves. It suggests that both the pure PS particles and core/shell particles in the latex colorants are formed from the same formation mechanism.

Encapsulation efficiency

Based on the method described in experimental section, encapsulation efficiencies of 79.8 and 78.2% were determined correspondingly for RBR and AF dyes while slightly high encapsulation efficiency, 84.2%, was reached for CBR dyes. It indicates that hydrophilic dyes, regardless of its chemical structure, have been mostly entrapped into PS matrix. On other words, about 20% of dyes enter into water and are not encapsulated. Reminding the fact that the hydrophilic dyes do not easily diffuse through the oil layer, those dyes existing in the external water phase should come from the miniemulsification stage, especially the ultrasonication stage for

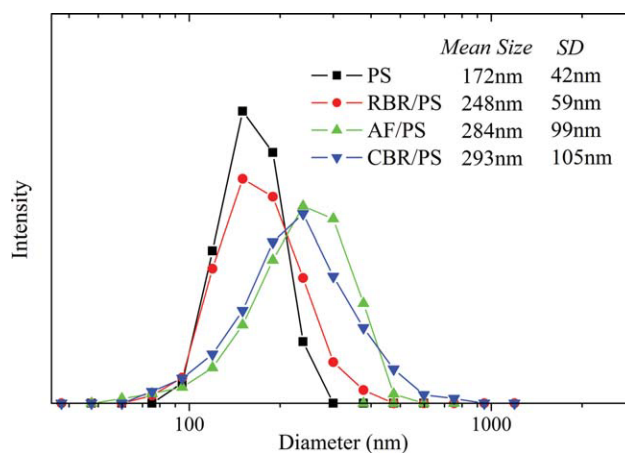


Figure 6 Particle size distributions of composite color latex and pure PS latex. The inserted data are the SDP intensity mean size and standard deviation (SD) of the lattices. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

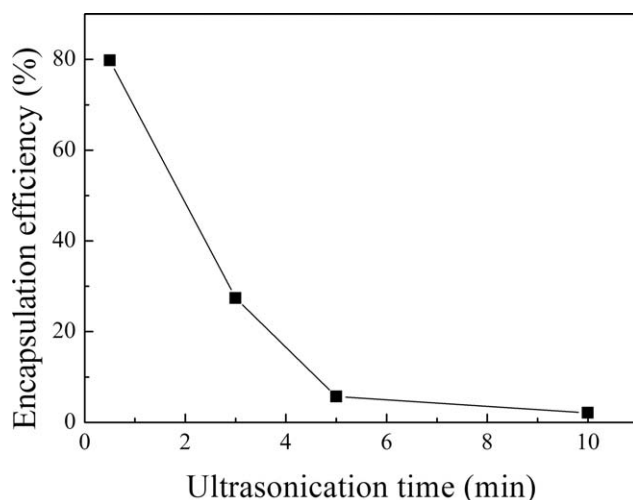


Figure 7 The encapsulation efficiency of RBR dye as a function of ultrasonication time.

formation of double miniemulsion, rather than from polymerization stage. Therefore, dependence of encapsulation efficiency on ultrasonication time was investigated, as shown in Figure 7. The encapsulation efficiency dramatically decreases from 79.8 to 2.1% as ultrasonication time increases from 0.5 to 10 min, suggesting that the dyes easily enter into external water phase during ultrasonication. This phenomenon could be interpreted from the formation mechanism of double miniemulsion, as schematically presented in Figure 8. The droplets, solely consisting of aqueous dye solution, in primary W/O miniemulsion were formed in a fashion similar to

conventional miniemulsions. However, when the primary W/O miniemulsion transformed into W/O/W double miniemulsion, two main kinds of droplets would occur. One consisted of styrene, octane, and HD [namely pure oil droplets, see Fig. 8(c)], and the other, besides styrene, octane, and HD, also contained a liquid core of aqueous dye solution [namely W/O droplets, see Fig. 8(c)]. Under ultrasonication, the fusion and fission among these droplets would take place with each other. Especially for the fission of W/O droplets, one droplet can be torn into one oil droplet and one small W/O droplet or into two oil droplets through disrupting the water core to release dye molecules to the external water phase. Unfortunately, these released dyes can not come back to the oil or W/O droplets any more due to their strong hydrophilicity. As ultrasonication time increased, more and more dyes transferred into external water phase and thus the encapsulation efficiency of dyes monotonously declines.

From the viewpoint of encapsulation efficiency, it seems that shorter ultrasonication time is benefit for the fabrication of dye/PS composite latex colorant. Nevertheless, egregiously short time leads to insufficient miniemulsification and thus large particle size and wide particle size distribution. Thus, the least ultrasonication time of 0.5 min was employed herein.

Water-fastness of the dye/PS composite colorants

The water-fastnesses of the obtained RBR/PS, AF/PS, and CBR/PS composite colorants were all

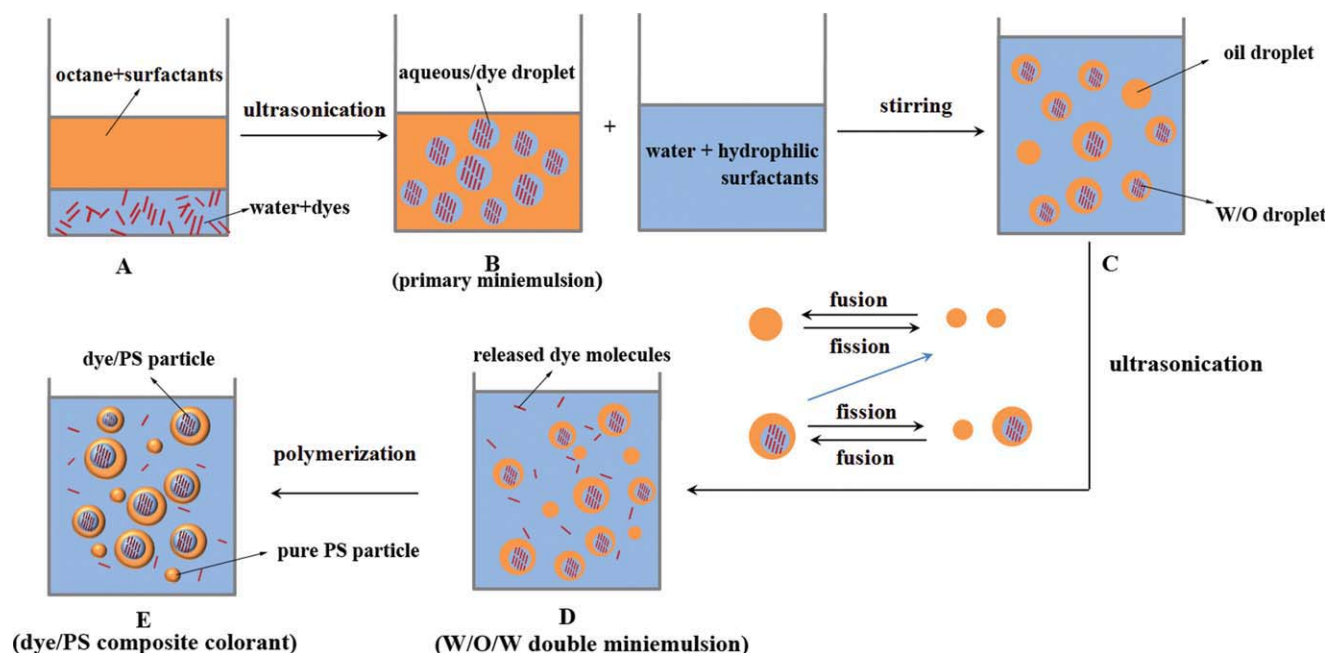


Figure 8 Schematic diagram of the formation mechanism of hydrophilic dyes/PS latex colorants using double miniemulsion technique. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

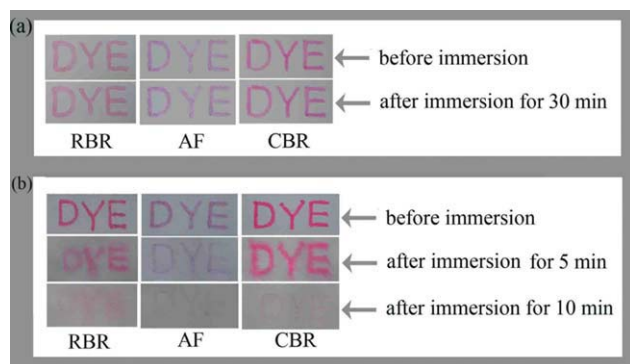


Figure 9 The disappearance of the words written with (a) dye/PS composite colorants and (b) the mixed colorants of dye with pure PS latex before and after immersion in water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

examined. Comparative experiments were carried out for the mixed colorants of dyes with pure PS latex. Those words, written with the composite colo-

rants and the mixed colorants, before and after immersion in water are shown in Figure 9. For the words written with the mixed colorants, they began to fade once wetted with water, and became blurry after immersion of 5 min and almost colorless after 10 min [see Fig. 9(b)]. However, for these words written with the three composite colorants, they do not have smearing or fading even after immersed in water for half an hour or longer [see Fig. 9(a)]. This confirms that encapsulation of hydrophilic dyes into PS shell can indeed efficiently improve the waterproofing property of the dyes.

Photostability of the composite latex colorants

Figure 10 presents the relative absorbance intensities of the dyes and the dye/PS composite colorants as a function of UV irradiation time. It can be seen that the absorption intensities quickly decrease as UV irradiation time increases for all three aqueous dye solutions. Especially for AF dye, only half

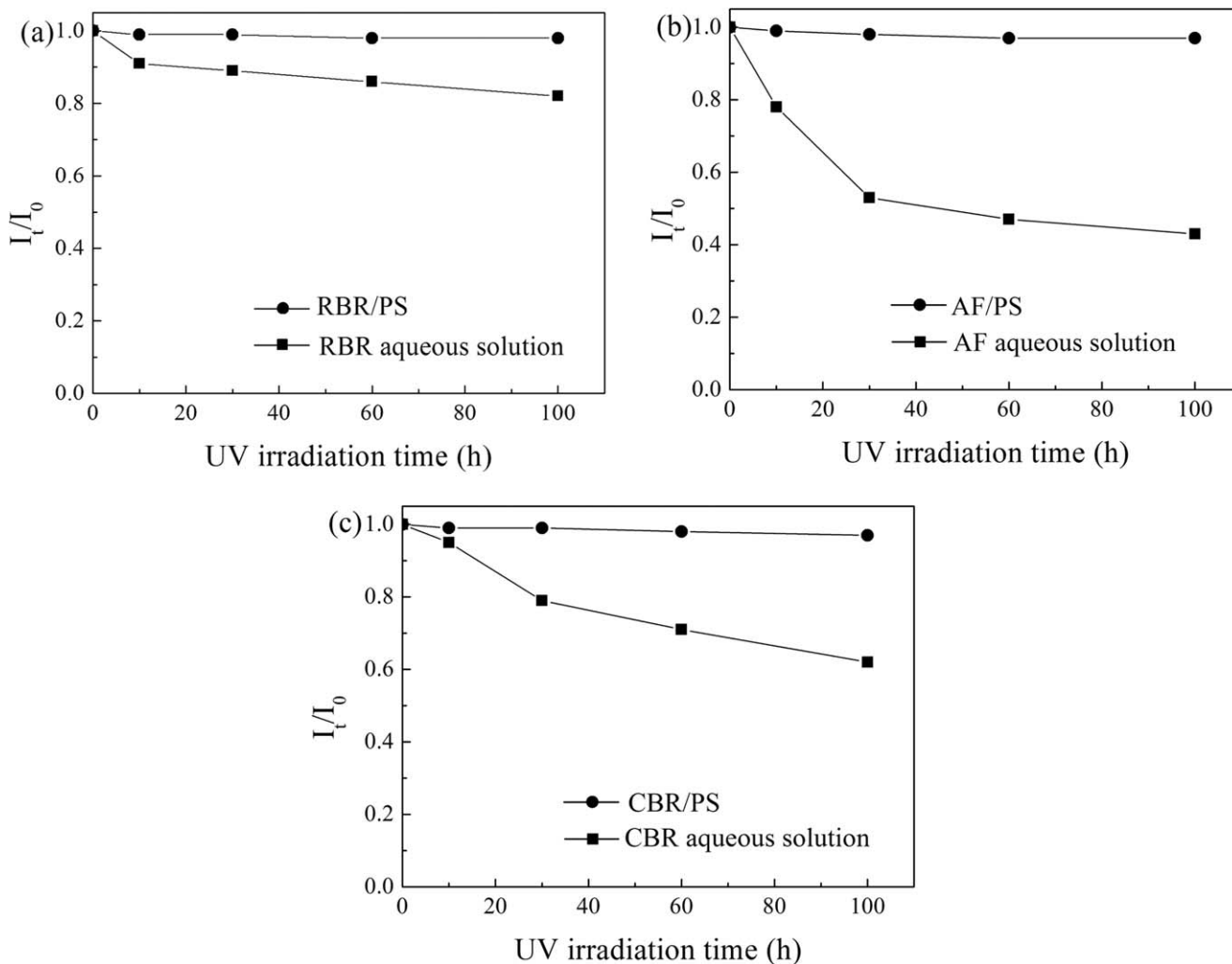


Figure 10 The relative absorption intensities of Dye/PS composite colorants and dye aqueous solutions as a function of UV irradiation time.

absorbance is left when the solution is exposed to UV lights for 100 h. In contrast to the quick lose of the color of the untreated dyes under UV irradiation, the absorption intensities of RBR/PS, AF/PS, and CBR/PS composite latex colorants decline very slightly even after 100 h of UV irradiation, indicating that the encapsulation of the hydrophilic dyes with PS can improve the photostability of the dyes considerably.

The better photostability of all of the end products could be explained by the single-photon photo-bleaching mechanism.²¹ Upon exposure to UV light at low irradiances and an ambient atmosphere, reactive singlet oxygen would be generated by the interaction between a dye's excited state and a ground-state oxygen molecule. The singlet oxygen would further oxidize dye molecules into colorless products. This photo-oxidation process is believed to be the main cause for the photo-fading of the dye molecules under UV irradiation with low intensity. In our cases, the incorporation of dye molecules into PS matrix means that the SDB dye molecules are protected from oxygen and the photo-oxidation of dyes are greatly reduced. Thus, the RBR/PS, AF/PS, and CBR/PS composite colorants exhibit improved photostability.

CONCLUSIONS

Three hydrophilic dyes with different molecular structures, that is, RBR, AF, and CBR, have been successfully encapsulated into PS particles using double miniemulsion method. Encapsulation efficiencies of 79.8, 78.2, and 84.2% are realized for RBR, AF, and CBR, respectively. Higher concentration of lipophilic emulsifiers in the primary miniemulsion and shorter ultrasonication time for the formation of double miniemulsion are favorable for the encapsulation of dyes. Besides, the aggregate state of dyes in water droplets may also contribute to the

efficient encapsulation of dyes. This encapsulation can obviously improve the water-proofing property and photostability of the organic dyes due to the core/shell structure. It is believed that the double miniemulsion process would be a universal technique to encapsulate hydrophilic dyes into polymer particles.

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